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(54) Name of Invention: Material for use in expansion molding and expansion molded products

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[Translator's note: All names need to be verified with the individual whose name it is.]

Specifications

1. Name of Invention

Material for use in expansion molding and expansion molded products

2. Claims

1. A material for use in expansion molding containing a polyvinyl cyclohexane resin and a foaming agent.

2. The material for use in expansion molding described in claim 1 in which a polyvinyl cyclohexane resin is obtained by the hydrogenation of a polymer or copolymer of a vinyl aromatic hydrocarbon compound.

3. The material for use in expansion molding described in claim 2 in which hydrogenation is set at a hydrogenation rate of 50% or above.

4. Expansion molded products obtained through expansion molding of the material for use in expansion molding described in claims 1, 2, or 3.

3. Detailed Explanation of the Invention

(Field of Industrial Applications)

This invention concerns a material for use in expansion molding which forms expansion molded products with superior heat resistance and weatherability, and, in particular, concerns material for use in expansion molding and expansion molded products which demonstrate excellent heat resistance and weatherability as covers for water and hot water pipes, and other such heat-insulating materials.

(Prior Art)

Styrene resin foams have many uses and, because of their superior heat resistance, are used for covers for water and hot water pipes and other such heat-insulating materials. However, because styrene resins are deficient in heat resistance, it has not been possible to use them for applications such as adiabatic thermal insulation of hot water pipes requiring heat resistance at the softening temperature and above of styrene family resins.

(Problems this Invention is to Solve)

Accordingly, in order to obtain a foam which would make use of the high plasticity of foaming polystyrene resins as well as be heat-resistant, we considered a method that would blend polymers with superior high resistance such as high density polyethylene and crystalline polypropylene, etc. However, there are problems with these polymers in that they do not have good compatibility with styrene resins and, because their retention of volatile foaming agents is also poor, there were problems such as either reduction in formability in the said blended product or the inability to obtain a good expansion molded body.

In addition, a method using a styrene–maleic anhydride copolymer has been offered (Tokai S 47 - 39186).

However, in addition to the fact that, because of the peculiar reaction of maleic anhydride in the manufacturing of this copolymer particle, an extremely complicated polymerization process is required, it is also necessary to use large amounts of maleic anhydride, which is not economical.

Furthermore, a foaming resin constituent which uses resin with methyl methacrylate as the main component and α - methyl styrene has the secondary component has been proposed, but, in this case, because the reactivity of α - methyl styrene is low, it is jointly used with a vinyl compound as a tertiary component and synthesis by suspension polymerization is carried out at high temperatures of 95 – 130° C with a polymerization period of approximately 20 minutes (Tokai S57 - 182334). Because of the high polymerization temperature and the length of time required, this is not economically feasible.

This invention does not have these sorts of problems and offers expansion molded products as well as a material for use in expansion modling which forms expansion molded products with excellent heat-resistance and weatherability and which are superior in terms of productivity and economic feasibility.

(Means for solving the problems)

Namely, this invention is related to a material for use in expansion molding containing polyvinyl cyclohexene resin and a foaming agent, as well as expansion molding products obtained by the expansion molding of the said material.

In this invention, the polyvinyl cyclohexane resin is a (co) polymer obtained by the addition of hydrogen to the aromatic hydrocarbon ring in a polymer or copolymer (below, (co) polymer) of vinyl aromatic hydrocarbon compound or a (co) polymer of a vinyl cyclohexane type compound. Among these, from the aspect of productivity and economic feasibility, a substance obtained by the hydrogenation (hydrogen addition) of a (co) polymer of vinyl aromatic hydrocarbon compound is preferable. In this case, hydrogenation of 50% or above of the aromatic hydrocarbon ring in the vinyl aromatic hydrocarbon compound (co) polymer is preferable, with hydrogenation of 70% or more particularly preferable. Here a hydrogenation rate of less than 50% will result in insufficient improvement in heat-resistance.

Furthermore, from the aspect of weatherability also, it is preferable for there to be few aromatic hydrocarbon rings. A high rate of hydrogenation gives superior weatherability.

Styrene, α - methyl styrene, o - methyl styrene, m - methyl styrene, p - methyl styrene, p - cyclohexyl styrene, p - t - butyl styrene, dimethyl styrene, α - vinyl naphthalene, β - vinyl naphtalene, α - isopropenyl naphthalene, β - isopropenyl naphthalene, metho oxystyrene, hydro oxystyrene, carbo methoxystyrene, acetoxystyrene, and cyano styrene can be given as examples of the vinyl aromatic hydrocarbon compound used, with styrene and α - methyl styrene being particularly suitable. It is possible to use the vinyl aromatic hydrocarbon compound either singularly or by mixing two or more types.

Moreover, it is also possible to use a copolymer that hydrogenizes a copolymer that is the copolymerization of another monomer that has copolymerization capability

with vinyl aromatic hydrocarbon compounds as the polyvinyl cyclohexene in this invention.

Unsaturated fatty acid ester, cyano vinyl compound, unsaturated dibasic acid and it derivatives, unsaturated fatty acid and its derivatives, etc. can be used as the monomer that has copolymerization capability with vinyl aromatic hydrocarbon compounds.

The following are examples of substances which are be used as the fatty acid ester: acrylic ester acrylates such as methyl acrylate, ethyl acrylate, butyl acrylate, 2 - ethylhexyl acrylate, etc.; cyclohexyl ester acrylates such as cyclohexyl acrylate, methyl cyclohexyl acrylate, bornyl acrylate, isobornyl acrylate, and adamantyl acrylate, etc.; aromatic ester acrylates such as phenyl acrylate, benzyl acrylate, and naphthyl acrylate, etc.; substituent aromatic ester acrylates such as flurophenyl acrylate, chlorophenyl acrylate, bromophenyl acrylate, flurobenzyl acrylate, chlorobenzyl acrylate, and bromobenzyl acrylate, etc.; halogenation alkylester acrylates such as fluoromethyl acrylate, fluoroethyl acrylate, chloroethyl acrylate, bromoethyl acrylate, etc.; ester acrylates such as hydrooxyalkyl ester acrylate, glycidyl acrylate, ethylene glycidyl ester acrylate, polyethylene glycol ester acrylate, alkyl amino alkyl ester acrylate, and cyano alkyl amino alkyl ester acrylate, etc.; α - substituent acrylic acid esters such as α - fluoro acrylic acid ester α - chloro acrylic acid ester, andr α - cyano acrylic acid ester, etc.; alkylester methacrylates such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, and 2 - ethyl hexyl methacrylate, etc.; aromatic ester methacrylates such as phenyl methacrylate, benzyl methacrylate, and naphthyl methacrylate, etc., substituent aromatic ester methacrylates such as flurophenyl methacrylate, chlorophenyl methacrylate, bromophenyl methacrylate, flurobenzyl methacrylate, chlorobenzyl methacrylate, and bromobenzyl methacrylate, etc.; halogenation alkylester methacrylates such as fluoromethyl methacrylate, fluoroethyl methacrylate, chloroethyl methacrylate, and bromoethyl methacrylate, etc.; ester methacrylates such as hydro oxyalkyl ester methacrylate, glycidyl methacrylate, ethylene glycol ester methacrylate,

polyethylene glycol ester methacrylate, alkyl amino alkyl ester methacrylate, and cyano alkyl ester methacrylate, etc., and alicyclic ester methacrylates such as cyclopentyl methacrylate, cyclohexyl methacrylate, methyl cyclohexyl methacrylate, trimethyl cyclohexyl methacrylate, norbornyl methacrylate, norbornyl methyl methacrylate, isobornyl methacrylate, bornyl methacrylate, menthyl methacrylate, phentyl methacrylate, adamantyl methacrylate, dimethyl adamantyl methacrylate, tricyclo [5.2.1.0^{2,6}] deca - 8 - ilu [translator's note: unverified] methacrylate, tricyclo [5.2.1.0^{2,6}] deca - 3 - methyl methacrylate, tricyclo [5.2.1.0^{2,6}] deca - 4 - methyl methacrylate, and cyclododecyl methacrylate.

Substances such as acrylonitrile and methacrylonitrile can be given as examples of the cyano vinyl compound.

Substances which can be given as examples of the unsaturated dibasic acid and its derivatives are N - substituent maleimides such as N - methyl maleimide, N - ethyl maleimide, N - propyl maleimide, N - butyl maleimide, N cyclohexyl maleimide, N - phenyl maleimide, N - methylphenyl maleimide, N - metylcyclohexyl maleimide, and N - carboxyphenyl maleimide, etc.; maleic acid and fumaric acid, etc. The following are examples of unsaturated fatty acids and their derivatives which can be used other than the previously mentioned unsaturated fatty acid esters: acrylic acid amides or methacrylic acid amide types such as acrylamide, methacrylamide, N - dimethacrylamide, N - diethylacrylamide, N - dimethacrylamide, and N - diethylmethacrylamide etc.; acrylate or methacrylate metals such as calcium acrylate, calcium methacrylate, barium acrylate, barium methacrylate, lead acrylate, lead methacrylate, tin acrylate, tin methacrylate, zinc acrylate, and zinc methacrylate, etc.; and acrylate and methacrylate. These can be used individually or, when two or more types are used, as a copolymer with a vinyl aromatic hydrocarbon compound.

Among other monomers with the capacity to form copolymers with these, acrylic acid ester, methacrylic acid ester, and N - substituent maleimide are preferred, with methyl methacrylate, methyl acrylate, norbornyl methacrylate, and tricyclo [5.2.1.0^{2,6}]

deca - 8 - ilu [translator's note: unverified] being particularly preferred.

The ratio of vinyl aromatic compound and another monomer which has the capacity to form a copolymer with this is preferably a weight ratio of the former to the latter of 5 – 100/95 – 0 (weight ratio), more preferably 10 – 100/90 – 0 (weight ratio), and most preferably 50 – 100/ 50 – 0.

Methods which can be used for manufacturing the (co) polymer of the vinyl aromatic hydrocarbon compound are generally known methods such as radical polymerization, ionic polymerization, and coordination polymerization, etc.

Methods which can be used as the radical polymerization method in order to obtain the previously mentioned polymer are generally known methods such as mass polymerization, suspension polymerization, emulsion polymerization and solution polymerization, etc.

The following are examples of the polymer initiator which can be used in the radical polymerization method: organic peroxides such as benzoyl peroxide, lauroyl peroxide, di-t-butyl peroxihexahydro terphthalate, t-butylperoxi-2-ethyl hexanolate, and 1,1-di-t-butylperoxi-3,3,5-trimethyl cyclohexane, etc.; azo compounds such as azobisisobutyronitrile, azobis-4-methoxy-2,4-dimethyl valerotolyl, azobis cyclohexanone-1-carbonytolyl, and azodibenzoyl, etc.; and water-soluble catalysts represented by potassium peroxide and ammonium peroxide, as well as redox catalysts which combine peroxides or peroxide salts and a reducing agent. Any of the usual substances which can be used in radical polymerization can also be used. It is preferable for the polymerization initiator to be used in a range of 0.01 – 10 weight % relative to the total amount of monomer. Polymer modifiers such as mercaptan compounds, thioglycol, carbon tetrabromide and α - methylstyrenedyma, etc. can be added as necessary for molecular weight modification.

For the polymerization temperature, it is preferable to select a suitable temperature between 0° and 200° C, with 50° – 120°C being particularly preferable.

The following can be used as the solvent in solution polymerization: benzene, toluene, xylene, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, and dichloroethylene, etc.

Suspension polymerization is carried out in a water medium and a suspension agent and suspension assistant are added as necessary. Water-soluble macro-molecules such as polyvinyl alcohol, methylcellulose, and polyacrylic amide, etc. and solubility-retardant inorganic materials such as calcium phosphate and magnesium pyrophosphate, etc. can be used as suspension agents. For the water-soluble macro-molecule type, it is preferable to use 0.03 – 1% by weight relative to the total amount of monomer and for the solubility-retardant inorganic material it is preferable to use 0.05 – 0.5% by weight relative to the total amount of monomer.

For the suspension assistant there are anionic surface active agents such as sodium dodecylbenzene sulfonate, etc., and, when using a solubility-retardant inorganic material as the suspension agent, it is preferable to jointly use a suspension assistant with the suspension agent. It is preferable to use 0.001 – 0.02 % by weight of the suspension assistant relative to the total amount of monomer.

Moreover, with anionic polymerization, it is possible to carry out manufacturing, in the presence of an initiator, usually at -80° – 200°C, preferably at 20° – 150°C, using methods such as mass polymerization, solution polymerization and slurry polymerization, etc. However, particularly when it is necessary to take into consideration the mixing of impurities into the resin and the elimination of reaction heat, solution polymerization using an inert solvent such as hexane or cyclohexane, etc. is preferable. Organic lithium compounds are usually used as the anionic polymerization initiator, but it is possible to suitably use n-butyl lithium, and sec-butyl lithium. Moreover, in this case, usually, as is well known, ethers and tertiary amine can also be added.

Furthermore, even used materials such as polystyrene foam molded products

and polystyrene molded materials can be used as the vinyl aromatic hydrocarbon compound (co) polymer used in this invention. In this case, the preferable method is one which makes it possible to plan for the re-use of material.

The (co)polymer obtained in this way is not particularly restricted as to its molecular weight, but from the perspective of heat-resistance and mechanical properties, a weight-average molecular weight (when measured using a standard calibration curve for polystyrene using gel permeation chromatography) within a range of 10,000 to 1,000,000 is preferable and substances within this range are particularly preferable when they are to be used as molded materials.

The hydrogenation of polymers of vinyl aromatic hydrocarbon compounds or copolymers of vinyl aromatic hydrocarbon compounds and monomers capable of being copolymerized with these, is carried out in the presence of a commonly known hydrogenation solvent, in a liquid phase that is either uniform or non-uniform. There are no particular restrictions on the solvent used at the time of the hydrogenation reaction, as long as it is inert in hydrogenation reactions, but ethers such as tetrahydrofuran and dioxane, alicyclic hydrocarbons such as cyclohexane and methyl cyclohexane, alcohols, and esters can be suitably used. The concentration of the polymer in the solution at the time of the hydrogenation reaction is 1 – 50% by weight. Economic feasibility is the reason this range is preferred.

The hydrogenation reaction is preferably carried out at temperatures of 10°C – 250°C, and hydrogen pressure of 1 kgf/cm^2 – 300 kgf/cm^2.

The metals nickel, cobalt, iron, titanium, rhodium, palladium, platinum, ruthenium or rhenium, their singular compounds or in combination of two or more can be used as the hydrogenation solvent, but the metals rhodium, palladium, platinum, ruthenium and rhenium or their compounds are particularly preferred because they made a hydrogenation reaction possible under mild reaction conditions. Solvents of an non-uniform type can be used as the metal or metal compounds themselves or carried

on suitable carriers. Ordinary carriers such as activated charcoal, silica, alumina, silica-alumina, diatomaceous earth, barium carbonate, calcium carbonate, titania, magnesia, zirconia, and silicon carbide, etc. can be used as the carrier. In this case, the amount of the above-mentioned metal carried on the carrier is usually within the range of 0.05 – 50% by weight, and preferably 0.05 – 20% by weight. Generally, methods which use a fixed bed, a suspension bed or a circulating style are good for non-uniform type hydrogenation reactions. Nickel, cobalt, titanium or iron compounds and organic methyl compounds, for example, organic alumi and solvents which combine organic lithium compounds, or organic metal complexes such as rhodium, palladium, platinum, ruthenium, and rhenium, etc. can be used as a uniform type solvent. The nickel, cobalt, titanium or iron compounds used in a uniform type solvent can be, for example, the metals acetylacetone salt, naphthenic acid salt, cyclopentadienyl compound, and cyclopentadienyldichloro compound. Alkyl aluminums such as triethyl aluminum and triisobutyl aluminum, etc., halogenation alkyl aluminums such as diethyl aluminum chlorolido, and ethyl aluminum dichlorolido, and aluminum hydrides such as diisobutyl aluminum [Translator's note: The last term in this compound is unverified. It sounds like hydolydo.] can be suitably used as the organic aluminum. Examples of organic metal complexes which can be used are , of the above-mentioned metal complexes, r-dichloro-π-benzene complex, dichloro tris (triphenylphosphine) complex, and hydrido [unverified] chloro tris (tripenylphophine), etc.

The polyvinyl styrene resin obtained by the addition of hydrogen can be recovered by any of the commonly known methods such as, for example, the steam slipping method, the direct release method, or the alcohol solidification method. The recovered polymer can then be used by being processed into a plate, etc.

Next, obtaining a polyvinyl styrene resin by (co) polymerizing a vinyl cyclohexane type compound will be explained.

Preferable methods to obtain, by polymer reaction, the vinyl cyclohexane resin to be used as the material for the vinyl cyclohexane compounds are cationic

polymerization and coordination polymerization.

In these methods, a polymer only of vinyl cyclohexane type compounds or a copolymer of a vinyl cyclohexane type compound based on a vinyl cyclohexane compound and other vinyl compound with which it has been copolymerized is obtained.

In the case of the copolymer, if the other vinyl compound is adjusted to be 50% or less by weight, a vinyl cyclohexane polymer containing a vinyl cyclohexane compound of 50% or above by weight will be obtained, which is preferable because of its superiority in improving heat resistance.

Examples of the substances which can be used as the vinyl cyclohexane type compound are vinyl cyclohexane, α - methyl vinyl cyclohexane, vinyl styrene cyclohexane, and vinyl butyl cyclohexane, etc. These can be used singularly or in mixtures of two or more.

Compounds such as those used as the previous vinyl aromatic compounds and copolymerized substances can be given as examples of the other vinyl compound to be copolymerized.

The usual cationic polymerization technology can be used as is as the method for cationic polymerization.

For example, using the previously mentioned compounds, it is possible to obtain a vinyl cyclohexane resin by solution polymerization at a polymerization temperature of 0°C or below, using a cationic polymerization catalyst such as tin chloride.

The usual coordination anionic polymerization technology can be used as is as the method for coordination anionic polymerization.

For example, using the previously mentioned compounds, it is possible to obtain a vinyl cyclohexane resin by polymerization at 0°C – 150°C, using a transition methyl catalyst such as titanium - triethyl aluminum tetrachloride.

Next, the foaming agent will be explained.

An easily volatile organic compound which does not dissolve the above-mentioned compounds and which is either a liquid or a gas at normal temperature and normal pressure can be used as the foaming agent in this invention. The following are examples which can be given: fatty aromatic hydrocarbons such as propane, butane, pentane, hexane and oil ether, etc.; cyclic hydrocarbons such as cyclohexane; and halogenation aromatic hydrocarbons such as methylene chloride, trichloro trifluro ethane, and dichloro difluro ethane, etc. The amount of foaming agent to be used is preferably within the range of 1 – 20 weight parts relative to 100 weight parts of polyvinylcyclohexane, and even more preferably, 2 – 12 weight parts.

At the time the polyvinylcyclohexane resin is impregnated with the foaming agent, a plasticizer can be present as necessary. An organic solvent capable of causing the dissolving or swelling of the polyvinylcyclohexane resin can be used as the plasticizer. Its boiling point is preferably a temperature of 150° C or below and approximately 10°C lower than the softening point of the polyvinyl cyclohexane. The following can be used as plasticizers: aromatic hydrocarbons such as ethyl benzine, toluene, styrene, benzine, and xylene; and halogenation hydrocarbons such as 1,2-dichloro propane, trichloroethylene, and tetrachloroethylene. It is preferable to use 0 – 5 % by weight of the plasticizer relative to the polyvinyl cyclohexane resin, and when a plasticizer is to be used, 0.5% by weight or above relative to the polyvinyl cyclohexane resin is preferable.

Moreover, thermal decomposition chemical foaming agents which produce gases such as N_2 gas or CO_2 gas by thermal decomposition can be used as foaming agents. These are substances such as azodicarbonamido, azobis isobutyronitrile, diazoaminobenzene, N,N' - dinitropentamehtylene tetramine, benzene sulfonylhydrazide, and trihydrozinotriazine, etc. It is preferable for these sorts of foaming agents to comprise 0.5 – 5% by weight relative to the polyvinyl cyclohexane resin.

In this invention, an easily volatile organic compound is used as the foaming agent and is impregnated into the polyvinyl cyclohexane resin by the following method. The particles of either sphere-form or plate-form of the polyvinyl cyclohexane resin in this invention are suspended in a water medium and the easily volatile organic compound is added to these. Impregnation under suspension conditions is preferably carried out at 90 – 130° C. In addition, another method in which the polyvinyl cyclohexane resin in this invention and the easily volatile organic compound are fusion mixed is also possible. In this case, an extruder is chiefly used.

When a thermal decomposition foaming agent is used, fusion mixing is done at a temperature at or below the decomposition temperature of the polyvinyl cyclohexane resin in this invention and the easily volatile organic compound. In this case too, an extruder is chiefly used.

Furthermore, the foaming of the material for use in expansion molding of this invention obtained in the way described above is done by methods such as pressure reduction. This method, which is a foaming and molding method for styrene resins widely carried out in industry, can be used as is. For example, in the case of resin particles, after preliminary foaming by water steam is done, the resin is further water steam foamed in a molding machine, making it possible to obtain a molded product. Moreover, it is also possible to obtain a molded body by using an extruding molding machine.

The foaming scale factor of the material for use in expansion molding in this invention can be freely selected from a low scale factor to a high scale factor.

The expansion molding products obtained from the material for use in expansion molding related to this invention can be used for such things as solar related insulation, hot water tank insulation, metal tile padding, food container insulation, insulation for use in vehicles and boats, hot water pipe insulation, air conditioner wind tunnels, sizing boards, construction materials related to automobiles, and simultaneous metal molding

panels, etc. and are particularly suitable for uses which require heat resistance and weatherability.

(Working Examples)

This invention will be explained below in even more detail by means of working examples. Furthermore, "%" indicates % by weight. Moreover, the measurement of physical properties was done according to the following methods.

<Manufacture of Preliminary Foaming Body>

The preliminary foam particles were obtained by heating foaming polymer particles with a particle diameter of 0.5 – 1.2 mm in 115°C steam for three minutes. After thermo-forming for 24 hours at room temperature, the preliminary foam particles were put in a 1 liter measuring cylinder and an apparent foam density (g/l) obtained.

<Molding of Foam Body>

The above-mentioned preliminary foam particles were loaded into a die with dimensions of height, 300 mm, width, 40 mm, thickness, 10 mm and after being steam heated in two conditions, 60 seconds and 120 seconds in each of the steams 0.6 $kg/cm^2 \cdot G$ (113°C), 0.8 $kg/cm^2 \cdot G$ (116°C), 1.0 $kg/cm^2 \cdot G$ (120°C), 1,25 $kg/cm^2 \cdot G$ (123°C), 1.50 $kg/cm^2 \cdot G$ (127°C), 1.75 (130°C) and 2.0 $kg/cm^2 \cdot G$ (133°C) in a table style autoclave, they were cooled and the foam body manufactured.

<Evaluation of Heat Resistance>

After molding in a table style autoclave, pressure and heating time in seconds at the beginning of shrinkage caused by steam were measured.

<Dimension Shrinkage>

A molded body which visually has a good finish and of which the inner part of the foam body has melted was cut into test pieces of 100 x 100 x 10 mm and, after drying for 24 hours at 50°C, left, without load, in a constant temperature drier at fixed

temperatures of 80°C, 85°C, 90°C, 95°C, 100°C, 105°C, 110°C, 115°C, 120°C, 125°C, and 130°C and changes in measurement obtained after 10, 40, 100 and 200 hours and the threshold temperature at which no dimension changes occurs obtained.

Working Example 1

After 0.6 g of benzoyl peroxioide [unverified] was dissolved in 500 g of styrene, this solution was put into a given autoclave to which had been added, respectively, 600 g of ion exchange water, 1 g of tricalcium phosphate, 3 g of water solution 0.5% dodecylbenzene sulfonate soda, and 0.3 g of sulfuric acid soda which are either dispersed or dissolved, and agitated at 270 rpm. The atmosphere inside the flask was replaced with nitrogen. Next, the temperature was raised to 85° C and polymerization carried out for 5 hours at this temperature and then continued for 3 hours at 98°C. After cooling, the polystyrene particles were removed, washed with hydrochloric acid and air dried. The weight-average molecular weight of the polystyrene was 32 x 10^4. Furthermore, in the working example, the weight-average molecular weight was measured using the standard calibration curve for polystyrene by the gel permeation chromatography method.

Five hundred grams of this polystyrene were dissolved in 5,000 g of cyclohexane, 75 g of stabilized Ni (activated charcoal carrier, 10% carrier rate) and 100 g of isopropyl alcohol mixed and agitated, and put into an autoclave. After the atmosphere inside the autoclave was replaced with nitrogen, the solution was agitated at an agitation rate of 900 rpm while being heated to 180°C. After this temperature increase, hydrogen gas was introduced from an automatic pressure regulator at a pressure of 100 kg/cm^2 and reacted for 8 hours. After cooling, it was diluted by adding 5,000 g of cyclohexane, and, after being put in a centrifuge, the Ni catalyst and the undissolved compounds were filtered out. The solution after filtering was dripped into 100 kg of methanol, the polyvinyl cyclohexane resin extracted, and, after separation from the solution, dried at reduced pressure. The molecular weight of the polyvinyl cyclohexane resin as a weight-average molecular weight of 12 x 10^4. The hydrogenation rate of close to 900 cm^{-1}

measured based on the absorption of infrared rays was almost 100%.

Next, the polyvinyl cyclohexane resin was heated to 240°C and made into plates with an extruder. Five hundred grams of the plates, 600 g of ion exchange water, 1 g of tricalcium phosphate, 3 g water solution 0.5% dodecylbenzene sulfonate soda, and 0.3 g of sulfuric acid soda were put into an autoclave and, while being agitated at 270 rpm, the temperature was elevated to 90°C. After temperature elevation, 5 g of toluene and 40 g of butane were added, the solution was heated at the same temperature for 8 hours, and, after agitation, it was cooled and foam polymer particles obtained. When a preliminary foaming of these foam polymer particles was done, the preliminary foam particles obtained an apparent density of 25 g/l. An expansion mold body was obtained using these preliminary foam particles. Its heat resistance was a steam pressure of 2.0 kg/cm^2 with a heating time of 120 seconds. The threshold temperature for dimension shrinkage of the expansion mold body was 120°C.

Working Example 2

Except for stopping the hydrogenation of the polystyrene at a hydrogenation rate of 59%, a polyvinyl cyclohexane resin was obtained by the same method as in working example 1. Using this resin, the preparation and testing of the foam polymer particles was the same as in working example 1. Heat resistance at an apparent density of the foam body of 29.4 g/l was 120 seconds of heating at a steam pressure of 2.0 kg/cm^2, dimension shrinkage (threshold temperature) was 110° C.

Working Example 3

After 0.6 g of benzoylperoxioide [unverified] was dissolved in a mixture of 350 g of styrene and 150 g of tricyclo $[5.2.1.0^{2,6}]$ deca - 8 -ilu, this solution was put into a given autoclave and agitated at 270 rpm after the addition by either dispersion or dissolving respectively of 600 g of ion exchange water, 1 g of tricalcium phosphate, 3 g of water solution 0.5 % dodecylbenzene and 0.3 g of sulfuric acid soda, and the atmosphere inside the autoclave was exchanged for nitrogen gas. Next, the temperature was

elevated to 70° C and polymerization carried out for five hours at this temperature and then continued for three hours at 98° C. After cooling, the polymer particles were taken out, washed with hydrochloric acid and air dried. The weight-average molecular weight of the polymer was 28×10^4. Five hundred grams of this polymer were dissolved in 5,000 g of cyclohexane and this solution was mixed and agitated with 75 g of stabilized Ni (activated charcoal carrier 10% carrier rate) and 100 g of isopropyl alcohol and put into an autoclave. After the atmosphere inside the autoclave was exchanged for nitrogen, while the solution was being agitated at an agitation rate of 900 rpm, the temperature was elevated to 180°C. After temperature elevation, hydrogen gas at a pressure of 100 kg/cm^2 was introduced from an automatic pressure regulator and reacted for eight hours. After cooling, the solution was diluted by the addition of 5,000 g of cyclohexane and after suspension in a centrifuge, the Ni catalyst and undissolved compounds were removed by filtering. The solution after filtering was dripped into 100 kg of methanol, the polyvinyl cyclohexane resin extracted, and, after separation from the solution, dried at reduced pressure. The molecular weight of the polyvinyl cyclohexane resin was a weight-average molecular weight of 21×10^4. The hydrogenation rate result of nearly 900 cm^{-1} measured based on infrared ray absorption was almost 98%.

Next the hydrogenated polymer was heated to 240° C and made into a plate with an extruder. Five hundred grams of this plate, 600 g of ion exchange water, 1 g of tricalcium phosphate, 3 g of water solution 0.5% dodecylbenzene, and 0.3 g of sulfuric acid were put into an autoclave and, while being agitated at 270 rpm, heated to 90° C. After temperature elevation, 5 g of toluene and 40 g of butane were added, and after 8 hours of heating to the same temperature and agitation, the solution was cooled and foam polymer particles obtained. After preliminary foaming of these foam polymer particles, preliminary foam particles with an apparent density of 35.7 g/l were obtained. An expansion molding body was obtained using these preliminary foam particles. Heat resistance was a heating period of 120 seconds at a steam pressure of 2.0 kg/cm^2. The dimension shrinkage of the expansion molding body was a threshold

temperature of 130° C.

Working Example 4

Other than using 300 g of styrene and 200 g of methyl methacrylate in place of 350 g of styrene and 150 g of tricyclo [5.2.1.$0^{2,6}$] deca - 8 -il, the preparation and testing of the foaming polymer particles was done in the same way as working example 3. The hydrogenation rate was 91%. The heat resistance of the foam body at an apparent density of 28.6 g/l was a heating period of 120 seconds at a steam pressure of 2.0 kg/cm^2 and the dimension shrinkage (threshold temperature) was 110° C.

Working Example 5

Other than using 100 g of styrene, 400 g of methyl methacrylate and 100 g of cyclohexyl maleimide in place of 350 g of styrene and 150 g of tricyclo [5.2.1.$0^{2,6}$] deca - 8 -il, the preparation and testing of the foaming polymer particles was done in the same way as working example 3. The hydrogenation rate was 100%. Heat resistance of the foam body at an apparent density of 24.1 g/l was a heating period of 120 seconds at a steam pressure of 2.0 kg/cm^2 and the dimension shrinkage (threshold temperature) was 115° C.

Comparative Example 1

Other than using a polystyrene with a hydrogenation rate of 0%, the preparation and testing of the foam polymer particles was carried out in the same way as working example 1. Heat resistance of this foam body at an apparent density of 27.2 g/l was a heating period of 60 seconds at steam pressure of 1.0 kg/cm^2, and dimension shrinkage (threshold temperature) was 80°C.

(Effects of the Invention)

The expansion molding products obtained by using the material for use in expansion molding which has the polyvinyl cyclohexane resin of this invention as a component is superior in heat resistance and weatherability, and is expected to be

widely used in areas which require these properties.

Moreover, because it is also possible to use expansion molded products of polystyrene which has been already once used as a material, this invention helps to conserve resources.

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